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(54) **SUBSTRATE PROCESSING APPARATUS, SUBSTRATE PROCESSING METHOD AND NON-TRANSITORY COMPUTER-READABLE RECORDING MEDIUM**

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(57) **ABSTRACT**

Described herein is a technique capable of acquiring, monitoring and recording the progress of the reaction between a substrate and a reactive gas contained in a process gas in a process chamber during the processing of the substrate. According to the technique, there is provided a substrate processing apparatus including: a process chamber accommodating a substrate; a process gas supply system configured to supply a process gas into the process chamber via a process gas supply pipe; an exhaust pipe configured to exhaust an inner atmosphere of the process chamber; a first gas concentration sensor configured to detect a first concentration of a reactive gas contained in the process gas in the process gas supply pipe; and a second gas concentration sensor configured to detect a second concentration of the reactive gas contained in an exhaust gas in the exhaust pipe.

15 Claims, 8 Drawing Sheets

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C23C 16/56	(2006.01)
C23C 16/455	(2006.01)
C23C 16/448	(2006.01)
H01L 21/31	(2006.01)
C23C 16/44	(2006.01)
H01J 37/32	(2006.01)

(52) **U.S. Cl.**
CPC ***C23C 16/4485*** (2013.01); ***C23C 16/45561*** (2013.01); ***C23C 16/56*** (2013.01); ***H01J 37/32449*** (2013.01); ***H01L 21/0262*** (2013.01); ***H01L 21/02164*** (2013.01); ***H01L 21/02222*** (2013.01); ***H01L 21/02282*** (2013.01); ***H01L 21/02326*** (2013.01); ***H01L 21/02337*** (2013.01); ***H01L 21/31*** (2013.01); ***H01L 21/67017*** (2013.01); ***H01L 21/67109*** (2013.01); ***H01L 21/67253*** (2013.01)

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See application file for complete search history.

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FIG. 1

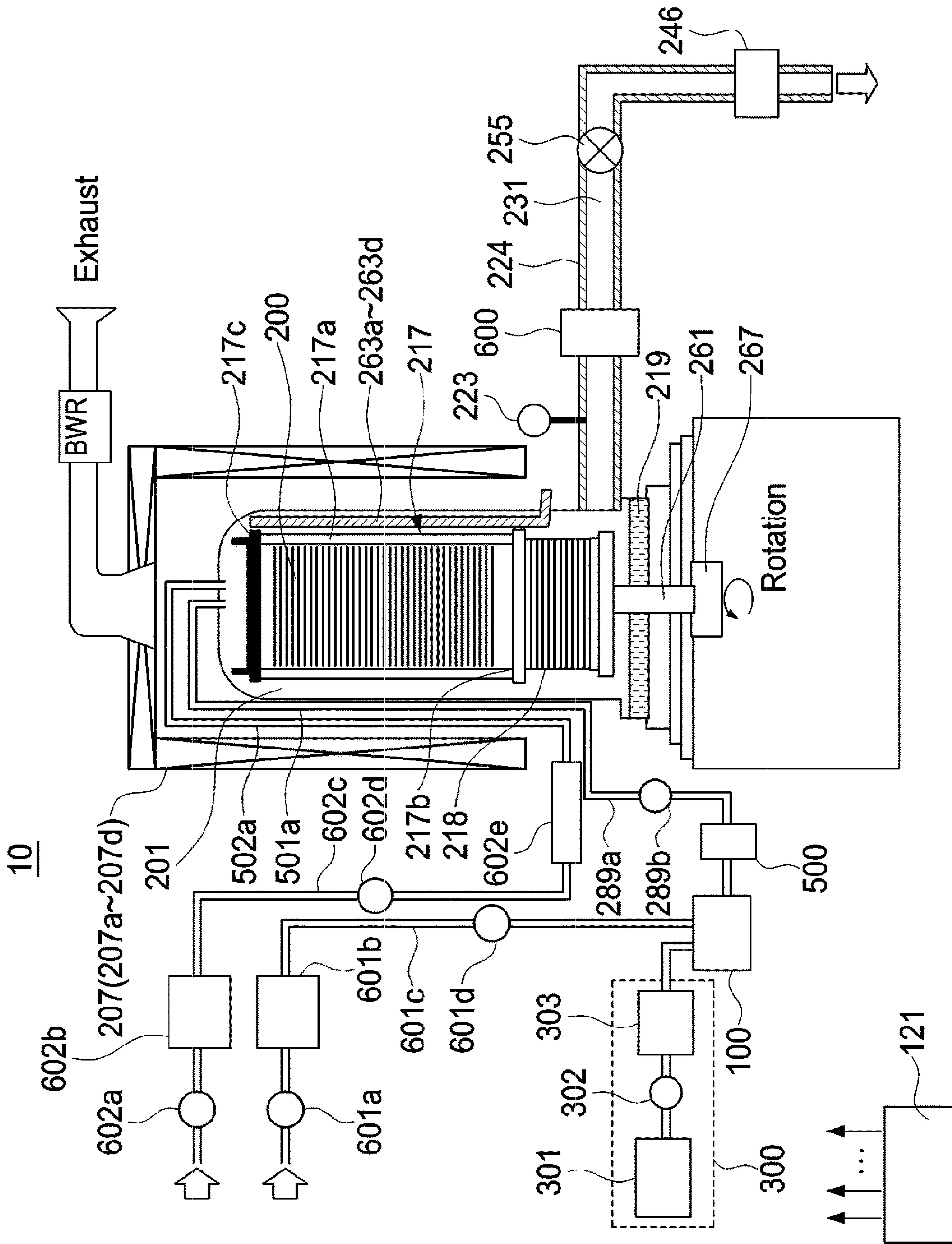


FIG. 2

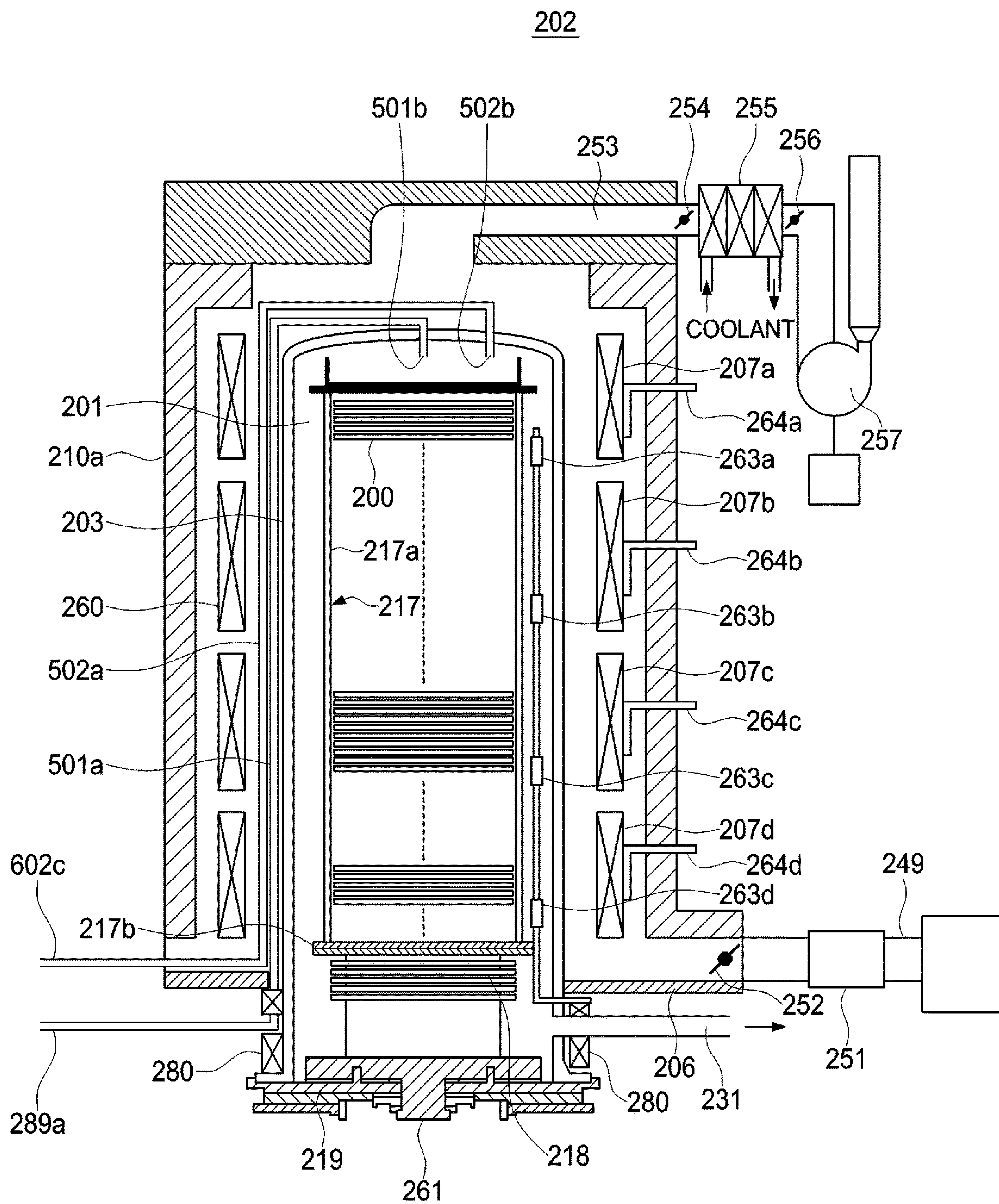


FIG. 3

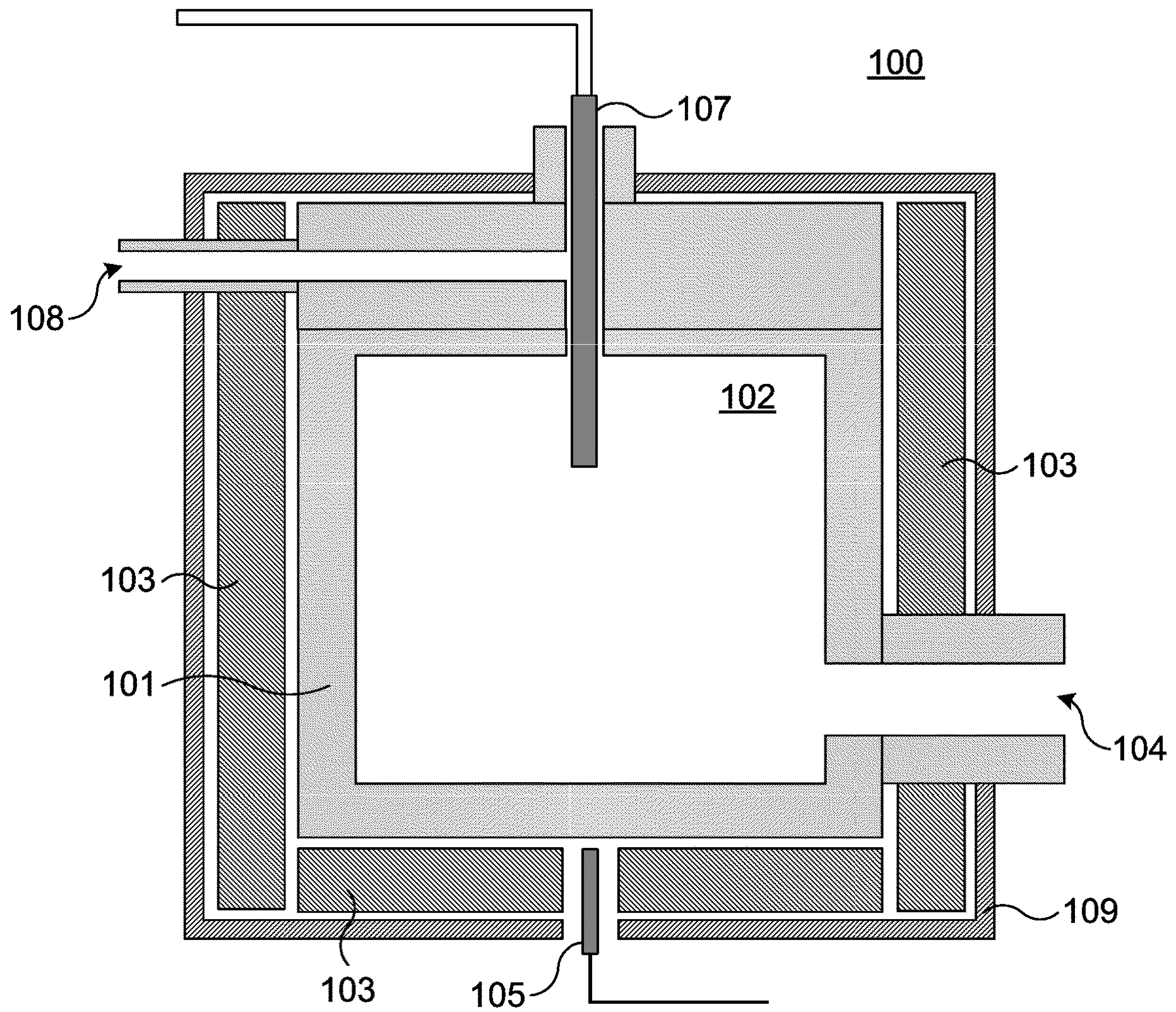


FIG. 4A

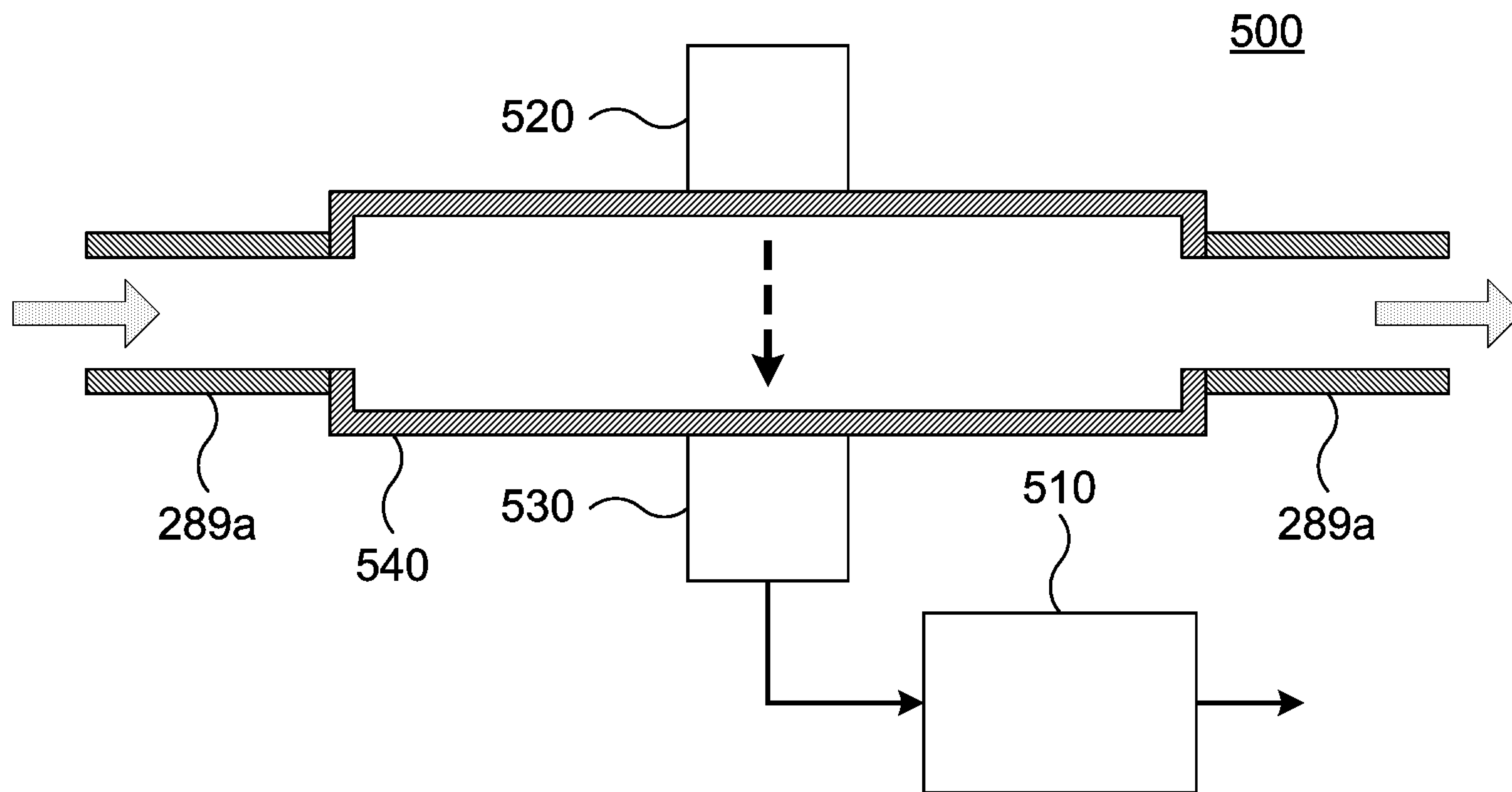


FIG. 4B

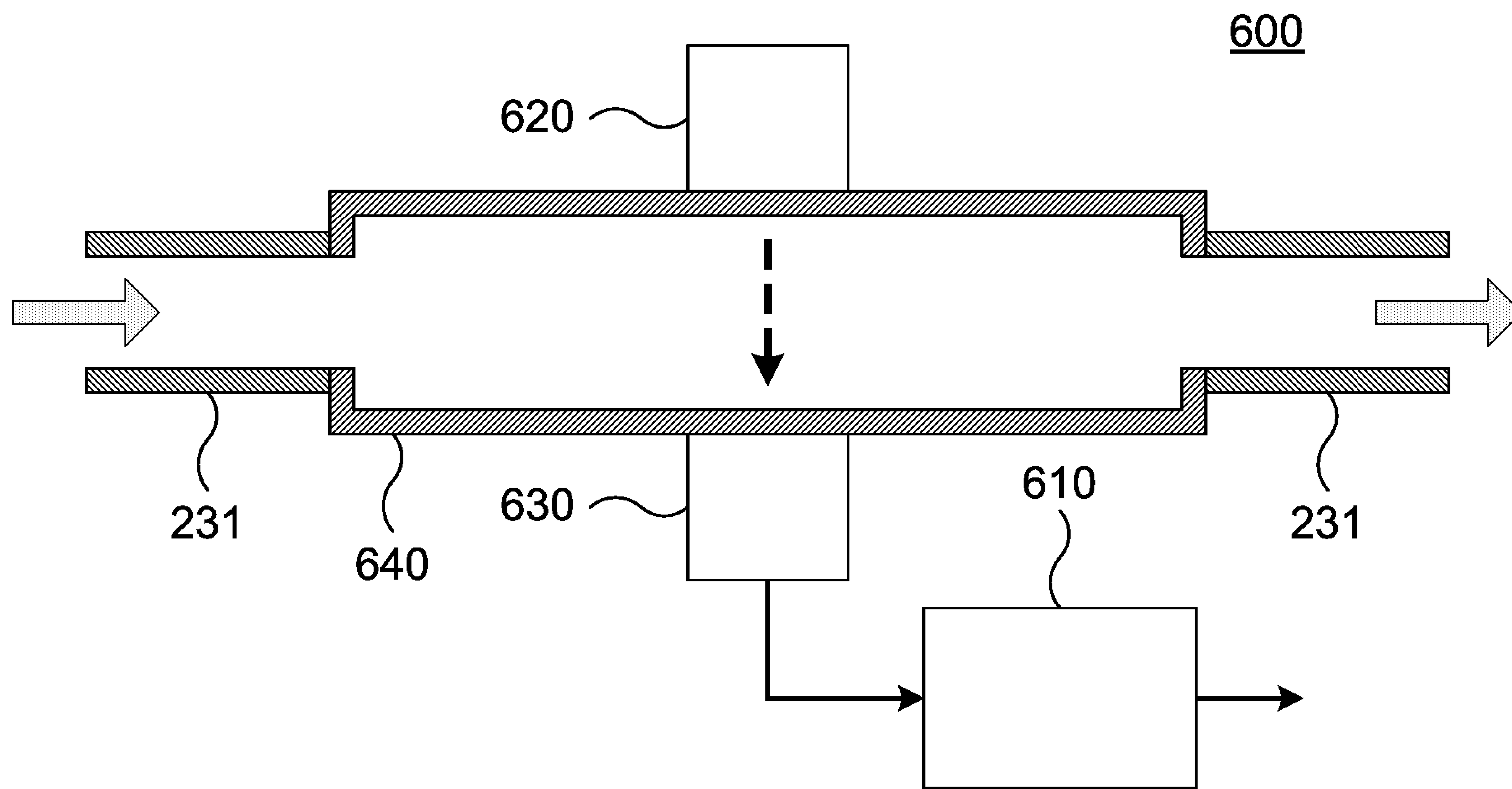


FIG. 5

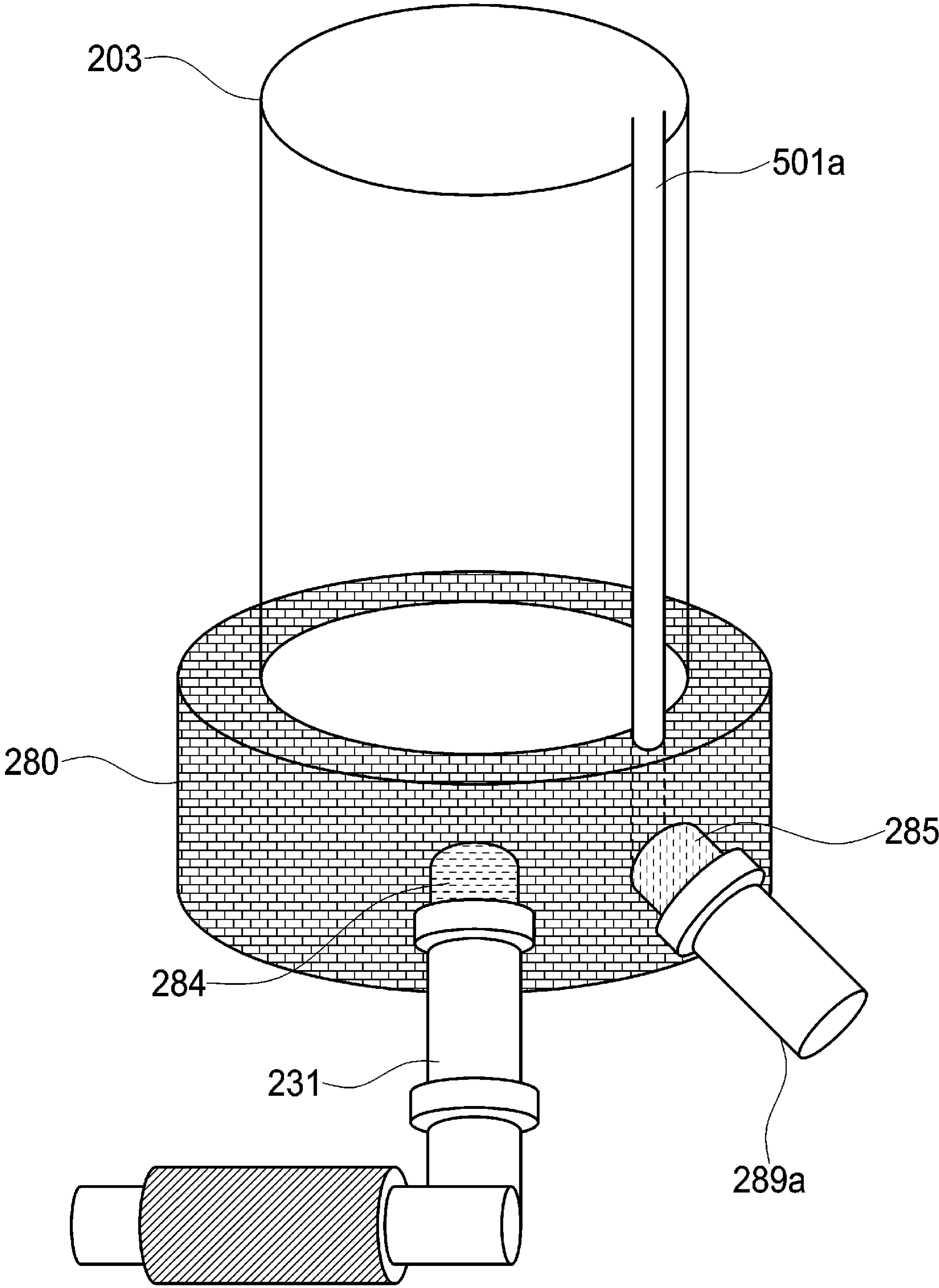


FIG. 6

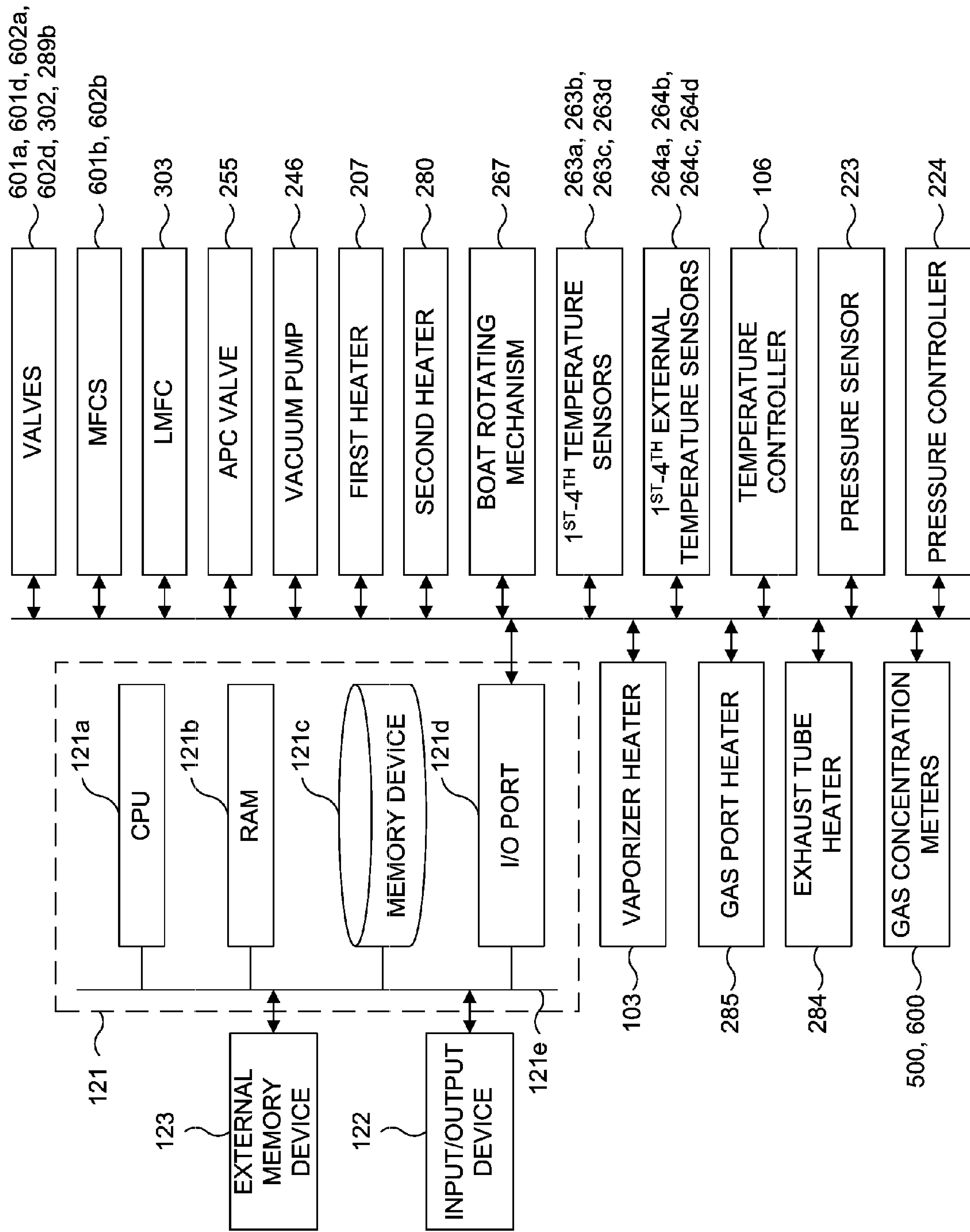


FIG. 7

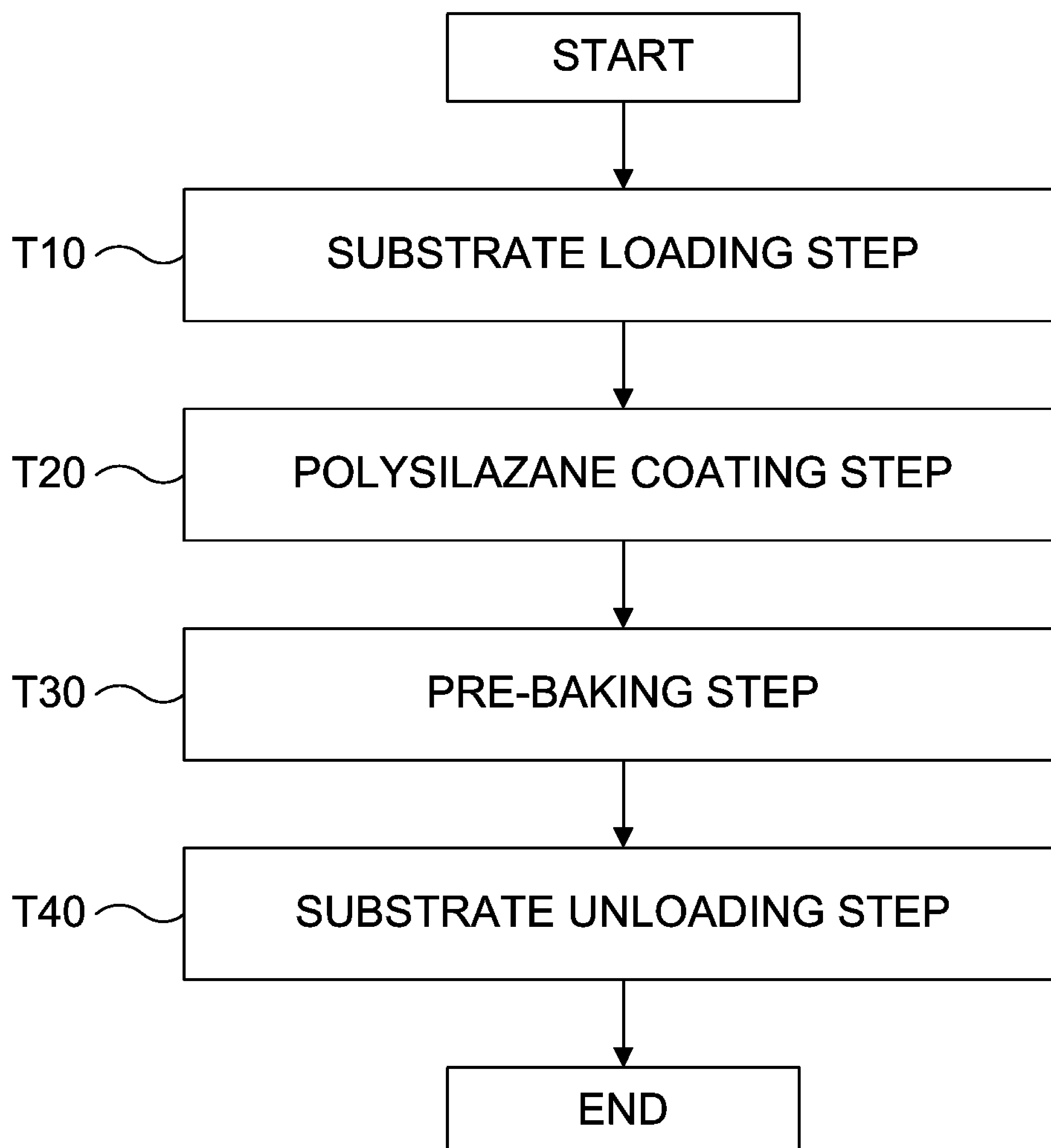
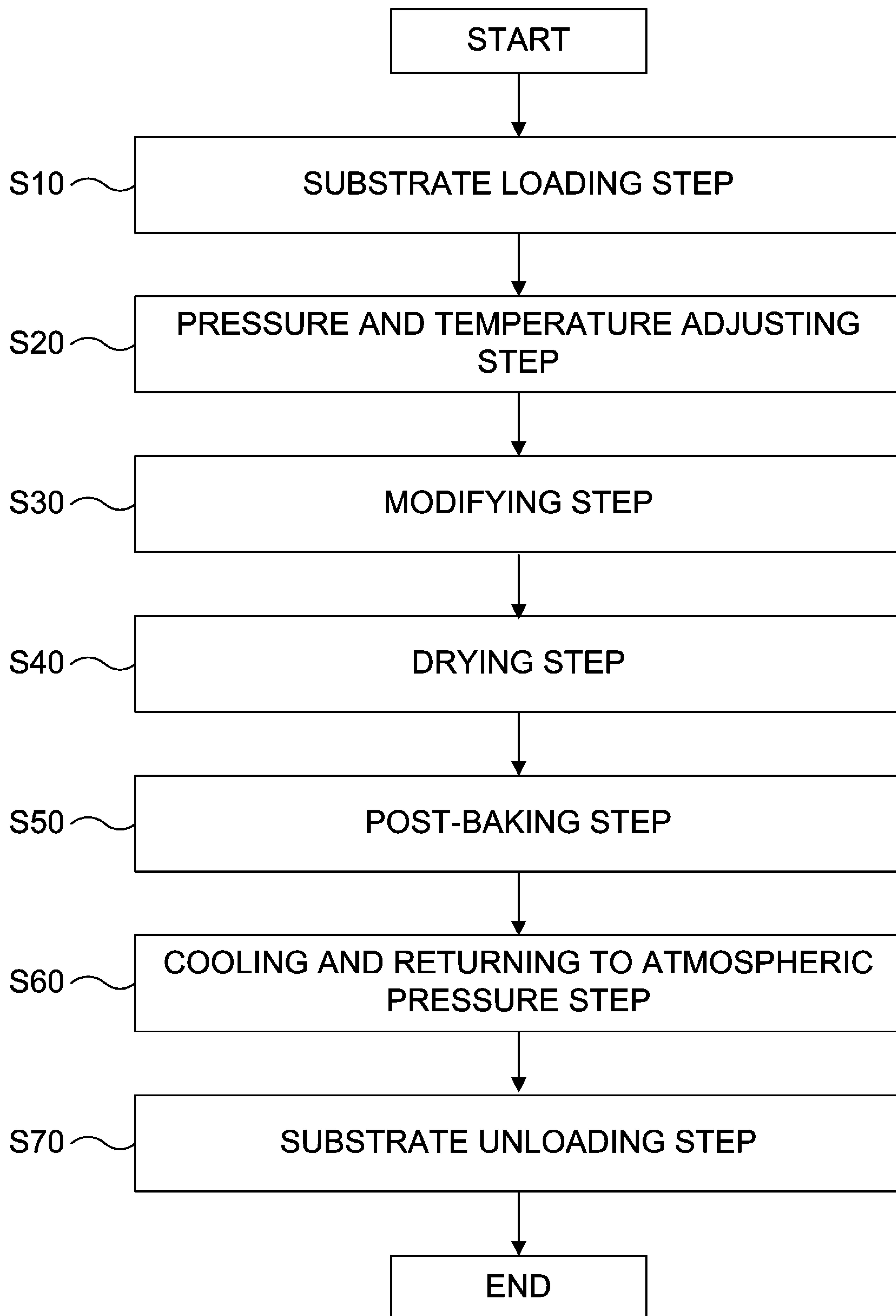


FIG. 8



SUBSTRATE PROCESSING APPARATUS, SUBSTRATE PROCESSING METHOD AND NON-TRANSITORY COMPUTER-READABLE RECORDING MEDIUM

CROSS-REFERENCE TO RELATED PATENT APPLICATION

This application is a continuation application of U.S. patent application Ser. No. 15/918,858, filed Mar. 12, 2018, which claims priority under 35 U.S.C. § 119 of International Patent Application No. PCT/JP2015/077502, filed on Sep. 29, 2015, the entire contents of which are hereby incorporated by reference.

BACKGROUND

1. Field

The present disclosure relates to a substrate processing apparatus.

2. Description of the Related Art

It is becoming more difficult to control interference between transistor devices due to leakage currents as the devices in a Large Scale Integrated circuit (hereinafter referred to as LSI) are miniaturized. The devices in the LSI are separated by forming voids such as grooves or holes in a silicon substrate and depositing an insulator in the voids. For example, an oxide film such as a silicon oxide film (SiO film) may be used as the insulator. The SiO film may be formed by oxidation of the silicon substrate, a chemical vapor deposition (CVD) method or a Spin-On-Dielectric (SOD) method.

Recently, with the miniaturization of devices, the technology of filling microstructures, especially filling deep or narrow voids with oxide, by the CVD method has reached its limit. In order to overcome the limits, a method of using an oxide having fluidity such as SOD ("SOD method") to fill the voids has been introduced. In the SOD method, an insulating coating material containing an inorganic component or an organic component called SOG (Spin-On-Glass) is used. The insulating coating material has been used in the manufacturing process of LSI before CVD oxide film was introduced. Since the manufacturing process of the LSI using the insulating coating material only requires 0.35 μm to 1 μm processes, the insulating coating material may be modified by performing the heat treatment at 400° C. under the nitrogen atmosphere. However, since latest manufacturing process of LSI such as DRAM (Dynamic Random Access Memory) and flash memory requires processes less than 50 nm processes, polysilazane (SiH_2NH) or PHPS (perhydropolysilazane) is used instead of SOG.

Polysilazane is a material obtained by catalytic reaction of dichlorosilane or trichlorosilane with ammonia, for example. A thin film may be formed by applying polysilazane on a substrate using a spin coater. The thickness of the coating film depends on the molecular weight and the viscosity of the polysilazane and the number of revolutions of the spin coater.

Polysilazane contains impurities such as nitrogen from ammonia used in the manufacturing process thereof. Therefore, it is necessary to remove impurities from the coating film (polysilazane film) by subjecting the polysilazane film to moisture and heat treatment after coating to obtain a dense oxide film. For example, moisture can be formed by reacting hydrogen and oxygen in a heat processing furnace to add moisture to the polysilazane film. The moisture permeates the polysilazane film and by heating the polysilazane film a dense oxide film is obtained. In case of STI (Shallow Trench Isolation), the maximum temperature of the heat treatment may be, for example, about 1,000° C.

While polysilazane has been widely used in LSI processes, it is necessary to reduce the thermal load of the transistor elements in order to prevent excessive diffusion of impurities such as boron, arsenic and phosphorus implanted in the transistor elements, to prevent the aggregation of metal silicide for electrode, to prevent the fluctuation of the performance of the work-function metal material for gate electrode, and to secure the number of read/write operations of the memory element. If moisture can be added efficiently, the thermal load can be easily reduced in the heat treatment performed after adding moisture.

Instead of filling the voids with insulator via the CVD method, the voids may be filled with insulator via a flowable CVD method.

In a substrate processing using a process gas, for example, in a process for obtaining a dense oxide film by modifying a polysilazane film coated by SOD or insulating material filled by a flowable CVD method, it is necessary to accurately acquire, monitor, and record the status of the substrate processing such as the progress of the substrate processing.

SUMMARY

Described herein is a technique capable of acquiring, monitoring and recording the progress of the reaction between a substrate and a reactive gas contained in a process gas in a process chamber during the processing of the substrate.

According to one aspect of the technique described herein, there is provided a substrate processing apparatus including: a process chamber capable of accommodating a substrate; a process gas supply system configured to supply a process gas into the process chamber via a process gas supply pipe; an exhaust pipe configured to exhaust an inner atmosphere of the process chamber; a gas concentration sensor configured to be capable of detecting a first concentration which is a concentration of the process gas in the process gas supply pipe and detecting a second concentration which is a concentration of the process gas contained in an exhaust gas in the exhaust pipe; and a controller configured to be capable of performing: (a) controlling the process gas supply system to start a supply of the process gas into the process chamber at a predetermined flow rate; and (b) controlling the process gas supply system to reduce the predetermined flow rate into the process chamber or to stop the supply of the process gas into the process chamber when an amount of the process gas consumed in the process chamber, which is calculated based on a value of the first concentration and a value of the second concentration detected by the gas concentration sensor, becomes equal to or lower than a predetermined value.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** schematically illustrates a vertical cross-section of a substrate processing apparatus according to an embodiment described herein.

FIG. **2** schematically illustrates a vertical cross-section of a processing furnace of the substrate processing apparatus according to the embodiment.

FIG. **3** schematically illustrates a vertical cross-section of a vaporizer of the substrate processing apparatus according to the embodiment.

FIG. **4**A schematically illustrates a vertical cross-section of a first gas concentration meter of the substrate processing apparatus according to the embodiment.

FIG. **4**B schematically illustrates a vertical cross-section of a second gas concentration meter of the substrate processing apparatus according to the embodiment.

FIG. **5** schematically illustrates a furnace opening and surroundings thereof of the processing furnace of the substrate processing apparatus according to the embodiment.

FIG. **6** schematically illustrates a configuration of a controller of the substrate processing apparatus and peripherals thereof according to the embodiment.

FIG. **7** is a flowchart illustrating a pre-processing performed before a substrate processing according to the embodiment.

FIG. **8** is a flowchart illustrating the substrate processing according to the embodiment.

EMBODIMENT

Hereinafter, an embodiment will be described with reference to FIGS. **1** through **8**.

(1) Configuration of Substrate Processing Apparatus

First, an example configuration of a substrate processing apparatus **10** in which a method of manufacturing a semiconductor device according to the embodiment is performed will be described with reference to FIGS. **1** and **2**. The substrate processing apparatus **10** is a device for processing a wafer (silicon substrate) **200** using a process gas generated by vaporizing a liquid containing hydrogen peroxide (H_2O_2) or a hydrogen peroxide solution. Preferably, the substrate processing apparatus **10** is capable of processing the wafer **200** having a concave-convex microstructure such as grooves. Specifically, the microstructure refers to a structure of high aspect ratio such as narrow grooves (concave structure) having a width of about 10 nm to 50 nm, for example. According to the embodiment, an oxide film is formed by filling the grooves with a polysilazane film, which is a silicon-containing film, and processing the polysilazane film with a process gas. While the embodiment will be described by way of an example in which a polysilazane film is processed by a process gas, the technique described herein is not limited to the polysilazane film. The techniques described herein may also be applied, for example, to the treatment of films including silicon, nitrogen and hydrogen, particularly films containing silazane bonds and plasma polymerized films of tetrasilylamine and ammonia.

<Processing Vessel>

As shown in FIG. **1**, a processing furnace **202** includes a processing vessel (reaction tube) **203**. The processing vessel **203** is made of a heat-resistant material such as quartz and silicon carbide (SiC), and is cylindrical with an open lower end. A process chamber **201** is provided in the hollow cylindrical portion of the processing vessel **203**. The process chamber **201** is capable of accommodating wafers (substrates) **200** charged in a boat **217**, which will be described later. The boat **217** supports concentrically arranged in vertical direction and horizontally oriented wafers **200**.

A seal cap **219**, which is a furnace opening cover capable of airtightly sealing the lower end opening (furnace opening) of the processing vessel **203**, is provided under the processing vessel **203**. The seal cap **219** is provided under the processing vessel **203** and is in contact with the lower end of the processing vessel **203**. The seal cap **219** is disk-shaped. The process chamber **201**, which is a processing space where the substrates are processed, is defined by the processing vessel **203** and the seal cap **219**

<Substrate Retainer>

The boat (substrate retainer) **217** supports concentrically arranged wafers **200** in vertical direction while each of the wafers **200** are in horizontal orientation. The boat **217** includes a plurality of support columns **217**a supporting the wafers **200**. The number of the support columns **217**a may be three, for example. The support columns **217**a are provided between a bottom plate **217**b and a top plate **217**c. The support columns **217**a support the concentrically arranged wafers **200** in multiple stages along the axis of the processing vessel **203**. The diameter of the top plate **217**c is greater than the diameter of each of the wafers **200**.

The columns **217**a, the bottom plate **217**b and the top plate **217**c are made of base metal having good thermal conductivity such as silicon carbide, aluminum oxide (AlO), aluminum nitride (AlN), silicon nitride (SiN) and zirconium oxide. Preferably, the columns **217**a, bottom plate **217**b and top plate **217**c are made of base metal with a thermal conductivity of at least 10 W/mK. In the case where the thermal conductivity is of no importance, the columns **217**a, the bottom plate **217**b and the top plate **217**c may be made of a material such as quartz. In case where the contamination of the wafer **200** by metal is of no importance, the columns **217**a and the top plate **217**c may be made of metal such as stainless steel (SUS). When the columns **217**a and the top plate **217**c are made of metal, a coating such as ceramic and Teflon (registered trademark) may be formed on the surface of the columns **217**a and the top plate **217**c.

An insulating body **218** is made of a heat-resistant material such as quartz and silicon carbide, and is provided under the boat **217**. The insulating body **218** prevents heat radiated from a first heater **207** from reaching the seal cap **219**. The insulating body **218** functions as a support body for supporting the boat **217** aw well as an insulating member. As shown in FIG. **2**, the insulating body **218** may be embodied by a plurality of disc-shaped insulating plates in horizontal orientation in multiple stages. However, the insulating body **218** is not limited thereto. For example, the insulating body **218** may be cylindrical quartz cap. The insulating body **218** may be regarded as one of the members constituting the boat **217**.

<Elevating Mechanism>

A boat elevator (not shown) is provided under the processing vessel **203**. The boat elevator is an elevating mechanism that loads the boat **217** into the processing vessel **203** and unloads the boat **217** out of the processing vessel **203** by lifting and lowering the boat **217**, respectively. When the boat **217** is elevated by the boat elevator, the seal cap **219** then airtightly closes the furnace opening.

A rotating mechanism **267** capable of rotating the boat **217** is provided at the seal cap **219** opposite to the process chamber **201**. A rotating shaft **261** of the rotating mechanism **267** is coupled to the boat **217** through the seal cap **219**. As the rotating mechanism **267** rotates the boat **217**, the wafers **200** are rotated.

<First Heater>

A first heater **207** is provided outside the processing vessel **203** and concentrically arranged with the processing vessel **203**. The first heater **207** is capable of heating the wafers **200** accommodated in the processing vessel **203**. The first heater **207** is supported by a heater base **206**. As shown in FIG. **2**, the first heater **207** includes a first heating part **207**a, a second heating part **207**b, a third heating part **207**c and a fourth heating part **207**d. The first heating part **207**a

through the fourth heating part **207***d* are provided in the processing vessel **203** along the stacking direction of the wafers **200**, respectively.

A first temperature sensor **263***a*, a second temperature sensor **263***b*, a third temperature sensor **263***c* and a fourth temperature sensors **263***d* are provided between the processing vessel **203** and the boat **217**, respectively. The first temperature sensor **263***a* through the fourth temperature sensor **263***d* are provided for the first heating part **207***a* through the fourth heating part **207***d*, respectively. The first temperature sensor **263***a* through the fourth temperature sensor **263***d* measures the temperature of the wafer **200** or ambient temperature, and each of the first temperature sensor **263***a* through the fourth temperature sensor **263***d* includes, for example, a thermocouple. The first temperature sensor **263***a* through the fourth temperature sensor **263***d* is capable of measuring the temperatures of wafers **200** at the center of each of the groups of wafers **200** heated by the first heating part **207***a* through the fourth heating part **207***d*.

The first heater **207** and the first temperature sensor **263***a* through the fourth temperature sensor **263***d* are electrically connected to a controller **121** which will be described later. The controller **121** controls the energization states of the first heating part **207***a* through the fourth heating part **207***d* based on the temperatures measured by the first temperature sensor **263***a* through the fourth temperature sensor **263***d* such that the wafers **200** in the processing vessel **203** are at a predetermined temperature. In addition, the controller **121** is also capable of independently controlling the energization state or the temperature of each of the first heating part **207***a* through the fourth heating part **207***d*. A first external temperature sensor **264***a*, a second external temperature sensor **264***b*, a third external temperature sensor **264***c* and a fourth external temperature sensor **264***d* may be further provided at the first heating part **207***a* through the fourth heating part **207***d*, respectively. The first external temperature sensor **264***a* through the fourth external temperature sensor **264***d* measures the temperatures of the first heating part **207***a* through the fourth heating part **207***d*, respectively, and each of the first external temperature sensor **264***a* through the fourth external temperature sensor **264***d* includes, for example, a thermocouple. The first external temperature sensor **264***a* through the fourth external temperature sensor **264***d* are connected to the controller **121** such that the controller **121** is able to monitor the temperature of each of the first heating part **207***a* through the fourth heating part **207***d* via the first external temperature sensor **264***a* through the fourth external temperature sensor **264***d*.

<Gas Supply Mechanism (Gas Supply System)>

As shown in FIGS. **1** and **2**, a process gas supply nozzle **501***a* and an oxygen-containing gas supply nozzle **502***a* are provided between the processing vessel **203** and the first heater **207** along the outer sidewall of the processing vessel **203**. For example, the process gas supply nozzle **501***a* and the oxygen-containing gas supply nozzle **502***a* are made of quartz which has a low thermal conductivity. The process gas supply nozzle **501***a* and the oxygen-containing gas supply nozzle **502***a* may have a double wall structure. Tips (downstream ends) of the process gas supply nozzle **501***a* and the oxygen-containing gas supply nozzle **502***a* are inserted into the processing vessel **203** through the ceiling of the processing vessel **203** in airtight manner. A supply hole **501***b* and a supply hole **502***b* are provided at the tips of the process gas supply nozzle **501***a* and the oxygen-containing gas supply nozzle **502***a* located in the processing vessel **203**, respectively. A process gas and an oxygen-containing gas are supplied into the processing vessel **203** toward the top plate **217***c* provided at the top of the boat **217** accommodated in the processing vessel **203** through the supply hole **501***b* and the supply hole **502***b*, respectively.

A gas supply pipe **602***c* is connected to the upstream end of the oxygen-containing gas supply nozzle **502***a*. A valve **602***a*, a mass flow controller (MFC) **602***b* which is a flow rate controller, a valve **602***d* and a heater **602***e* capable of heating a gas are provided at the gas supply pipe **602***c* in order from the upstream side to the downstream side of the gas supply pipe **602***c*. For example, the oxygen-containing gas includes oxygen (O_2) gas, ozone (O_3) gas, nitrous oxide (NO_2) gas and combinations thereof. In the embodiment, O_2 gas is used as the oxygen-containing gas. The heater **602***e* is capable of heating the oxygen-containing gas to 80° C. to 150° C. It is preferable that the oxygen-containing gas is heated to 100° C. to 120° C. The heater **602***e* assists the heating of the process gas supplied into the process chamber **201** by heating the oxygen-containing gas. In addition, the re-liquefaction of the process gas in the processing vessel **203** may be suppressed. Further, the oxygen-containing gas may be heated by the first heater **207**.

Instead of the oxygen-containing gas, a gas having low reactivity with the wafers **200** or the film formed on the wafers **200** may be supplied through the oxygen-containing gas supply nozzle **502***a*. For example, nitrogen (N_2) gas or rare gases such as argon (Ar) gas, helium (He) gas and neon (Ne) gas may be supplied through the oxygen-containing gas supply nozzle **502***a*. The process gas supply nozzle **501***a* and the oxygen-containing gas supply nozzle **502***a* extend along the inner sidewall to the top portion of the processing vessel **203**, and lower ends of the process gas supply nozzle **501***a* and the oxygen-containing gas supply nozzle **502***a* penetrate the lower portion of the processing vessel **203** in airtight manner. At least one gas ejecting hole (gas supply hole) is provided either at the portion of the process gas supply nozzle **501***a* or the portion of the oxygen-containing gas supply nozzle **502***a* or both extending along the sidewall of the processing vessel **203**. The gas may be supplied through the at least one gas ejecting hole (gas supply hole) parallel to the wafer **200**.

A downstream end of a process gas supply pipe **289***a* for supplying the process gas is connected to the upstream end of the process gas supply nozzle **501***a*. A vaporizer **100**, which is process gas generator capable of generating the process gas by vaporizing the liquid source, a gas concentration meter (gas concentration sensor) **500**, a valve **289***b* and a gas port heater **285** are provided at the process gas supply pipe **289***a* in order from the upstream side to the downstream side of the process gas supply pipe **289***a*. According to the embodiment, a gas containing at least H_2O_2 gas is used as the process gas. A pipe heater (not shown) such as a jacket heater is provided around the process gas supply pipe **289***a* to heat the process gas supply pipe **289***a*. As shown in FIG. **5**, the gas port heater **285** is provided at a connecting portion between the process gas supply nozzle **501***a* and the process gas supply pipe **289***a*, and is configured to heat the process gas passing through the connecting portion. In case the process gas supply nozzle **501***a* is inserted into the processing vessel **203** through the lower portion thereof, it is preferable that the gas port heater **285** is provided outside the processing vessel **203** whereat the process gas supply nozzle **501***a* is inserted.

A liquid source supply system (liquid source supply mechanism) **300** for supplying a liquid source (a liquid containing hydrogen peroxide) of the process gas to the

vaporizer **100** and a carrier gas supply system (carrier gas supply mechanism) (not shown) are connected to the vaporizer **100**.

The liquid source supply system **300** may include a liquid source supply **300**, a valve and a liquid mass flow controller (LMFC) **300** for controlling the flow rate of the liquid source supplied to the vaporizer **100** provided in order from the upstream side to the downstream side of the liquid source supply system **300**.

The carrier gas supply system may include a carrier gas supply pipe **601***c*, a carrier gas valve **601***a*, an MFC **601***b* which is a carrier gas flow rate controller and a carrier gas valve **601***d*. According to the embodiment, the oxygen-containing gas such as O2 gas may be used as the carrier gas. However, the oxygen-containing gas may include O3 gas, NO gas as well as O2 gas and combinations thereof which may be used as the carrier gas. Further, gases having low reactivity with the wafers **200** or films formed on the wafers **200** may be used as the carrier gas. For example, nitrogen (N_2) gas or rare gases such as argon (Ar) gas, helium (He) gas and neon (Ne) gas may be used as the carrier gas.

According to the embodiment, the process gas supply nozzle **501***a* and the supply hole **501***b* constitute a process gas supply system. The process gas supply system may further include the process gas supply pipe **289***a*, the valve **289***b*, the gas concentration meter **500** and the vaporizer **100**. The oxygen-containing gas supply nozzle **502***a* and the supply hole **502***b* constitute an oxygen-containing gas supply system. The oxygen-containing gas supply system may further include the gas supply pipe **602***c*, the heater **602***e*, the valve **602***d*, the MFC **602***b* and the valve **602***a*. The process gas supply system and the oxygen-containing gas supply system constitute the gas supply system (gas supply mechanism).

<Vaporizer>

FIG. **3** schematically illustrates a configuration of the vaporizer **100**. The vaporizer **100** vaporizes the liquid source by dropping the liquid source onto a heated member. The vaporizer **100** includes: a vaporizer vessel **101** which is the heated member, and defines a vaporizing space **102**; a vaporizer heater **103** for heating the vaporizer vessel **101**; an outlet port **104** for exhausting (supplying) the gas obtained by vaporizing the liquid source to the process gas supply pipe **289***a* as a process gas; a thermocouple (temperature sensor) **105** for measuring the temperature of the vaporizer vessel **101**; a temperature controller **106** for controlling the temperature of the vaporizer heater **103** based on the temperature measured by the thermocouple **105**; a dripping nozzle **107** which is a liquid supply unit for supplying the hydrogen peroxide solution supplied from the LMFC **303** into the vaporizer vessel **101**; and a carrier gas inlet port **108** for supplying a carrier gas supplied through the carrier gas supply pipe **601***c* into the vaporizer vessel **101**.

The vaporizer vessel **101** is heated by the vaporizer heater **103** such that that the dripped liquid source is vaporized as it reaches the inner surface of the vaporizer vessel **101**. A thermal insulator **109** may be provided to improve the efficiency of the vaporizer heater **103** heating the vaporizer vessel **101** or to insulate the vaporizer **100** and other components. In order to prevent the vaporizer vessel **101** from reacting with the liquid source, the vaporizer vessel **101** is made of a material such as quartz and SiC. The temperature of the vaporizer vessel **101** may be lowered by the temperature or vaporization heat of the dripped liquid source. Therefore, it is preferable that the vaporizer vessel **101** is made of a material having a high thermal conductivity such as SiC in order to minimize the temperature fluctuation of the vaporizer vessel **101**.

According to the embodiment, a liquid source which is a mixture of two or more sources having different boiling points such as a hydrogen peroxide solution are heated and vaporized by the vaporizer **100**. Even when the liquid source is heated to a temperature higher than the boiling point of the liquid source, one of the one or more sources having a lower boiling point may be vaporized first and the rest of the one or more sources having higher boiling points may not be vaporized unless the liquid source is uniformly heated. As a result, the concentration ratio among the one or more sources in the vaporized gas may not be uniform since the rest of the one or more sources having higher boiling points may be concentrated in the liquid source.

More specifically, the hydrogen peroxide solution is the mixture of H_2O_2 and H_2O. Therefore, the boiling point of the hydrogen peroxide solution depends on the concentration of H_2O_2. For example, the boiling point of pure hydrogen peroxide (H_2O_2 concentration of 100%) is about 150° C. under atmospheric pressure, and the boiling point of a hydrogen peroxide solution with a H_2O_2 concentration of 34% is about 106° C. under atmospheric pressure. Therefore, when the hydrogen peroxide solution supplied to the vaporizer vessel **101** is vaporized, the water (H_2O) in the hydrogen peroxide solution is first vaporized unless the vaporizer vessel **101** is uniformly heated. As a result, H_2O_2 may be concentrated in the hydrogen peroxide solution.

Therefore, according to the embodiment, by rapidly heating the entire hydrogen peroxide solution on the heating surface of the vaporizer vessel **100** to a temperature higher than the boiling point of the hydrogen peroxide solution having a boiling point higher than water, the concentration of hydrogen peroxide is suppressed. More specifically, for example, when vaporizing a hydrogen peroxide solution with a H_2O_2 concentration of 34%, the vaporizer heater **103** heats the vaporizer vessel **101** to a temperature higher than the boiling point of the hydrogen peroxide solution. By dripping the hydrogen peroxide solution onto the heated surface of the vaporizer vessel **101**, the droplets of the hydrogen peroxide solution are rapidly heated and vaporized at a temperature higher than 106° C. The vaporizer heater **103** is capable of heating the vaporizer vessel **101** to a temperature higher than the boiling point of 150° C. of pure hydrogen peroxide with a H_2O_2 concentration of 100% such that H_2O_2 in hydrogen peroxide solution is prevented from concentrating when vaporized.

However, the decomposition of H_2O_2 is accelerated as the heating temperature rises. Therefore, it is necessary for the hydrogen peroxide solution to be heated to as low a temperature as possible while also preventing H_2O_2 from concentrating. In particular, H_2O_2 decomposes rapidly when the temperature exceeds 150° C. Thus, according to the embodiment, the temperature of the vaporization heater **103** is controlled to a temperature as high as the boiling point of the hydrogen peroxide solution of a predetermined concentration, but as low as possible to prevent the concentration of H_2O_2.

<Exhaust System>

One end of a gas exhaust pipe **231** for exhausting the inner atmosphere of the process chamber **201** is connected to the lower sidewall of the processing vessel **203**. A vacuum pump, which is a vacuum exhausting device, is connected to the other end of the gas exhaust pipe **231** via a gas concentration meter (gas concentration sensor) **600** and an APC (Automatic Pressure Controller) valve **255** which is a pres-

sure controlling device. The inner atmosphere of the process chamber **201** is exhausted by way of generating negative pressure by a vacuum pump **246**. The APC valve **255** may be opened or closed to vacuum-exhausting the process chamber **201** or stop the vacuum exhaust. The opening degree of the APC valve **255** may be adjusted in order to control the inner pressure of the process chamber **201**. A pressure sensor **223**, which is a pressure detector, is provided at the upstream side of the APC valve **255**. The inner pressure of the process chamber **201** may be exhausted to a predetermined pressure (vacuum level) by using above-described components. A pressure controller **224** shown in FIG. **6** is electrically connected to the pressure sensor **223** and the APC valve **255**. The pressure controller **224** controls the operation of the APC valve **255** such that the inner pressure of the process chamber **201** is adjusted to a desired level at a desired timing based on the pressure detected by the pressure sensor **223**.

The gas exhaust pipe **231** and the APC valve **255** constitute the exhaust system. The exhaust system may further include the gas concentration meter **600** and the pressure sensor **223**. The exhaust system may further include the vacuum pump **246**.

<Gas Concentration Meter (Gas Concentration Sensor)>

The gas concentration meter **500** is provided at the process gas supply pipe **289***a*. The gas concentration meter **500** measures (detects) the concentration of the process gas flowing in the process gas supply pipe **289***a* supplied from the vaporizer **100**. The gas concentration meter **600** is provided at the gas exhaust pipe **231**. The gas concentration meter **600** measures (detects) the concentration of the exhaust gas flowing in the gas exhaust pipe **231** which is exhausted from the process chamber **201**. In the embodiment, the concentrations of the gases measured by the gas concentration meters **500** and **600** refer to the concentrations of certain gases contained in the process gas and the exhaust gas, respectively. For example, the certain gases include a reactive gas contained in the process gas for processing the wafers **200** such as H_2O_2 gas for oxidizing the silicon-containing film formed on the wafers **200**. That is, the gas concentration meter **500** measures (detects) the concentration of the H_2O_2 gas contained in the process gas and the gas concentration meter **600** measures (detects) the concentration of the H_2O_2 gas contained in the exhaust gas.

As shown in FIG. **4**A, the gas concentration meter **500** includes a cell **540** through which the process gas supplied via a process gas supply pipe **289***a* passes; a light emitter **520** for irradiating a light beam, particularly a near-infrared ray, to the process gas passing through the cell **540**; a light receiver **530** for receiving the light beam irradiated from the light emitter **520** and passed through the process gas in the cell **540**; and an analyzer (gas concentration calculator) **510** for analyzing the spectrum of the light beam received by the light receiver **530** and calculating the concentration of H_2O_2 in the process gas. Similarly, as shown in FIG. **4**A, the gas concentration meter **600** includes a cell **640** through which the exhaust gas supplied via the gas exhaust pipe **231** passes; a light emitter **620** for irradiating a light beam, particularly a near-infrared ray, to the exhaust gas passing through the cell **640**; a light receiver **630** for receiving the light beam irradiated from the light emitter **620** and passed through the exhaust gas in the cell **640**; and an analyzer (gas concentration calculator) **610** for analyzing the spectrum of the light beam received by the light receiver **630** and calculating the concentration of H_2O_2 in the exhaust gas. The analyzers **510** and **610** are connected to the light receivers **530** and **630**, respectively, via, for example, optical fibers, and analyze the spectrum of the light beam received by the light receivers **530** and **630**. The analyzers **510** and **610** the concentrations of H_2O_2 in the process gas and exhaust gas, respectively, by evaluating the magnitudes of the unique spectral component of the light beam passed through the process gas or exhaust gas containing the H_2O_2 in the cells **540** and **640**. The concentration data of the H_2O_2 calculated by the analyzers **510** and **610** are transmitted to the controller **121**. Although the analyzers **510** and **610** according to the embodiment are described as calculating the concentration of the H_2O_2, the analyzers **510** and **610** may calculate other data representing the concentration of the H_2O_2 rather than the concentration of the gas itself

<Second Heater>

When a gas containing H_2O_2 (reactive material) obtained by vaporizing a hydrogen peroxide solution (aqueous solution containing H_2O_2) or by converting the hydrogen peroxide solution into mist state is used as the process gas, it is possible that the gas containing H_2O_2 is cooled down to a temperature lower than the boiling point of H_2O_2 in the processing vessel **203**, resulting in the re-liquefaction of H_2O_2 or the re-liquefaction of gas containing H_2O_2.

Specifically, the re-liquefaction of the gas containing H_2O_2 may occur in a region of the processing vessel **203** other than the region of the processing vessel **203** heated by the first heater **207**. As described above, the first heater **207** heats the region of the processing vessel **203** in which the wafer **200** is present since the first heater **207** is provided to heat the wafer **200** in the processing vessel **203**. However, the region other than where the wafer **200** is present may not be adequately heated by the first heater **207**. As a result, the region other than the region heated by the first heater **207** may be a low temperature region in which the gas containing H_2O_2 may be cooled and re-liquefied when passing through.

The liquid from the re-liquefaction of the gas containing the H_2O_2 may remain at the bottom of the processing vessel **203** (the upper surface of the seal cap **219**), which may result in a chemical reaction between the liquid and the seal cap **219** to damage the seal cap **219**. The liquid remaining on the seal cap **219** may also flow out of the processing vessel **203** through the furnace opening (the opening at the lower end of the processing vessel **203**) when the seal cap **219** is lowered to open the furnace opening of the processing vessel **203** in order to unload the boat **217** from the processing vessel **203**. As a result, the members around the furnace opening of the processing furnace **202** may be also damaged and the safety of the operator around the processing furnace **202** cannot be secured.

The liquid from the re-liquefaction of the gas containing the H_2O_2 may have higher H_2O_2 concentration than the hydrogen peroxide solution supplied into the processing vessel **203**. The liquid from the re-liquefaction of the gas containing the H_2O_2 may be re-vaporized in the processing vessel **203**. As described above, since the boiling point of H_2O_2 differs from that of H_2O, and H_2O is first vaporized, the gas produced by re-vaporization may have higher H_2O_2 concentration than the gas supplied into the processing vessel **203**.

Thus, the H_2O_2 concentration of the gas produced by re-vaporization and the concentration of the gas containing the H_2O_2 supplied into the processing vessel **203** may not be uniform. As a result, the substrate processing may not be uniform among the wafers **200** in the processing vessel **203**, and the characteristics of the substrate processing may deviate for each wafer **200**. In addition, the substrate processing may deviate for each lot of wafers **200**. Moreover, as the re-liquefaction and re-vaporization of H_2O_2 are repeated,

the concentration of H_2O_2 may become higher. As a result, the possibility of explosion or combustion may increase.

In order to solve the above-described problems, a second heater **280** is provided in the processing furnace **202** as shown in FIGS. **2** and **5**. The second heater **280** is capable of heating the region other than the region heated by the first heater **207**. That is, the second heater **280** is provided concentric with the processing vessel **203** to surround the outer side surface (outer periphery) of the lower portion (around the furnace opening portion) of the processing vessel **203**.

The second heater **280** is capable of heating the gas containing H_2O_2, which flows from the upstream side to the downstream side of the processing vessel **203** toward the exhaust unit, at the lower region of the processing vessel **203** where the insulating body **218** is provided. The second heater **280** is also capable of heating members in the lower region of the processing vessel **203** such as the seal cap **219** for sealing the lower end opening of the processing vessel **203** and the insulating body **218** provided at the bottom of the processing vessel **203**. The second heater **280** is provided lower than the bottom plate **217***b* when the boat **217** is loaded into the process chamber **201**. The second heater **280** may be embodied by a lamp heater, for example.

The controller **121**, which will be described later, is electrically connected to the second heater **280**. The controller **121** controls the energization state of the second heater **280** at a predetermined timing such that the inner temperature of the processing vessel **203** is at a temperature (e.g., 100° C. to 300° C.) high enough to suppress liquefaction of the process gas (i.e., the gas including H_2O_2). The second heater **280** continues to heat the furnace opening of the processing vessel **203** at least during the supply of the process gas into the processing vessel **203**. Preferably, the second heater **280** continues to heat the furnace opening of the processing vessel **203** from the loading of the wafer **200** into the processing vessel **203** until the unloading of the wafer **200** from the processing vessel **203**. As a result, the re-liquefaction of the process gas at the furnace opening and attachment of particles and impurities generated in drying process, which will be described later, to the furnace opening may be prevented. By starting to heat the furnace opening by the second heater **280** after the wafer **200** is loaded, the time required to prepare for the pre-processing before the supply of the process gas is shortened.

As described above, the gas port heater **285** is provided at the connecting portion between the process gas supply nozzle **501***a* and the process gas supply pipe **289***a*. The gas port heater **285** is capable of heating the process gas passing through the connecting portion. The gas port heater **285** is controlled to be at a desired temperature such that condensation does not occur in the process gas supply pipe **289***a*. For example, the gas port heater **285** is controlled to be at a temperature ranging from 50° C. to 300° C. An exhaust tube heater **284** is provided at the connecting part between the gas exhaust pipe **231** and the processing vessel **203**. The exhaust tube heater **284** is controlled to be at a desired temperature such that condensation does not occur in the gas exhaust pipe **231**. Preferably, the exhaust tube heater **284** is controlled to be at a temperature ranging from 50° C. to 300° C.

<Controller>

As shown in FIG. **6**, the controller **121**, which is a control device (control means), may be embodied by a computer having a CPU (Central Processing Unit) **121***a*, a RAM (Random Access Memory) **121***b*, a memory device **121***c* and an I/O port **121***d*. The RAM **121***b*, the memory device **121***c* and the I/O port **121***d* may exchange data with the CPU **121***a* via an internal bus **121***e*. An input/output device **121** such as a touch panel and a display device may be connected to the controller **121**.

The memory device **121***c* may be embodied by components such as flash memory and HDD (Hard Disk Drive). A control program for controlling the operation of the substrate processing apparatus **10** and a process recipe in which information such as the order and condition of the substrate processing which will be described later is stored are readably stored in the memory device **121***c*. The process recipe is a program that is executed in the controller **121** to obtain a predetermined result by performing sequences of the substrate processing. Hereinafter, the process recipe and the control program are collectively referred to simply as a program. The term "program" may refer to only the process recipe, only the control program, or both. The RAM **121***b* is a work area in which the program or the data such as the calculation data and the processing data read by the CPU **121***a* are temporarily stored.

The I/O port **121***d* is electrically connected to the components such as the LMFC **303**, the MFCs **601***b* and **602***b*, the valves **601***a*, **601***d*, **602***a*, **602***d*, **302** and **289***b*, the APC valve **255**, the first heater **207** (the first heating part **207***a* through the fourth heating part **207***d*), the second heater **280**, the first temperature sensor **263***a* through the fourth temperature sensor **263***d*, the rotating mechanism **267**, the pressure sensor **223**, the temperature controller **106**, the gas concentration meters **500** and **600**, and the pipe heater (not shown).

The CPU **121***a* is configured to read and execute the control program stored in the memory device **121***c*, and read the process recipe stored in the memory device **121***c* in accordance with an instruction such as an operation command inputted via the input/output device **122**. The CPU **260***a* may be configured to control operation of the substrate processing apparatus **10** according to the process recipe. For example, the CPU **260***a* may be configured to perform operation such as a flow rate adjusting operation of the LMFC **303** for the liquid source, flow rate adjusting operations of the MFCs **601***a* and **601***b* for various gases, opening/closing operations of the valves **601***a*, **601***d*, **602***a*, **602***d*, **302** and **289***b*, an opening/closing operation of the APC valve **255**, a temperature adjusting operation of the first heater **207** based on the temperatures measured by the first temperature sensor **263***a* through the fourth temperature sensor **263***d*, a temperature adjusting operation of the second heater **280**, a start and stop of the vacuum pump **246**, a rotation speed adjusting operation of the boat rotating mechanism **267**, a temperature adjusting operation of the vaporizer heater via the temperature controller **106**, and a temperature adjusting operation of the pipe heater. The CPU **260***a* may be configured to analyze gas concentration data obtained by the gas concentration meters **500** and **600**, which will be described later.

The controller **121** may be embodied by installing the above-described program stored in an external memory device **123** to a computer. The external memory device **123** may include a magnetic tape, a magnetic disk such as a flexible disk and a hard disk, an optical disk such as CD and DVD, a magneto-optical disk such as MO, and a semiconductor memory such as a USB memory and a memory card. The memory device **121***c* or the external memory device **123** may be embodied by a non-transitory computer readable recording medium. Hereafter, the memory device **121***c* and the external memory device **123** are collectively referred to as recording media. Herein, "recording media" may refer to only the memory device **121***c*, only the external memory

device **123**, or both. In addition to the external memory device **123**, a communication network such as the Internet and dedicated line may be used as the means for providing the program to the computer.

(2) Pre-Processing

Hereinafter, the pre-processing performed before the modifying step of the wafer (substrate) **200** will be described with reference to FIG. **7**. As shown in FIG. **7**, the pre-processing includes: a polysilazane coating step T**20** wherein polysilazane is coated on the wafer **200**; and a pre-baking step T**30**. According to the polysilazane coating step T**20**, the polysilazane is applied by a spin coater (not shown). The thickness of the coated polysilazane is determined by the conditions such as the molecular weight of the polysilazane, the viscosity of the polysilazane solution and the number of revolutions of the spin coater. According to the pre-baking step T**30**, the solvent is removed from the polysilazane coated on the wafer **200**. Specifically, the solvent is volatilized by heating the polysilazane coated on the wafer **200** to a temperature of from about 70° C. to 250° C. Preferably, the polysilazane coated on the wafer **200** is heated to about 150° C.

The wafer **200** used in the pre-processing has a concave-convex microstructure. The applied polysilazane fills at least the grooves of the concave-convex structure. That is, polysilazane coating film, which is a silicon-containing film, is formed in the grooves of the wafer (substrate) **200**. Hereinafter, an example wherein a gas containing H_2O_2, which is obtained by vaporizing a hydrogen peroxide solution, is used as a process gas will be described. The silicon-containing film is a film containing, for example, silicon, nitrogen and hydrogen. The silicon-containing film may also contain carbon or other impurities. "Microstructure" refers to a structure with a high aspect ratio such as deep grooves or narrow grooves of about 10 nm to 30 nm formed on a silicon substrate, for example.

In the pre-processing according to the embodiment, the wafer **200** is loaded (substrate loading process, T**10**) into a processing apparatus (not shown) which is different from the substrate processing apparatus **10** described above, and the polysilazane coating step T**20** and the pre-baking step T**30** are performed in the processing apparatus. The wafer **200** is unloaded (substrate take-out step, T**40**) from the processing apparatus. However, in the pre-processing, the polysilazane coating step T**20** and the pre-baking step T**30** may be performed by two separate apparatuses.

(3) Substrate Processing

Next, an exemplary sequence of the substrate processing for manufacturing a semiconductor device will be described with reference to FIG. **8**. A modifying step according to the embodiment wherein a silicon-containing film formed on the wafer (substrate) **200** is modified into an SiO film using a process gas containing H_2O_2 will be described. Herein, the components of the substrate processing apparatus **10** are controlled by the controller **121**.

Since hydrogen peroxide (H_2O_2) has higher activation energy and has more oxygen atoms in one molecule than water vapor (H_2O), hydrogen peroxide (H_2O_2) is stronger oxidant than water vapor (H_2O). Therefore, by using a gas containing H_2O_2 as the process gas, the oxygen atoms can reach the film formed at the bottoms of the grooves of the wafer **200**. As a result, the modification step may be performed more uniformly between the convex portion of the film and concave portion of the film at the bottom of the grooves of the wafer **200**. As a result, the dielectric constant of the wafer **200** after the modifying step is more uniform. Since the modifying step may be performed at a low temperature, problems such as deterioration of the performance of the circuit formed on the wafer **200** may be suppressed. According to the embodiment, the reactant H_2O_2 vaporized or converted to be in mist state (H_2O_2 in the gaseous phase) is referred to as a "H_2O_2 gas" or a "reactive gas" and a gas containing at least H_2O_2 gas is referred to as "process gas." An aqueous solution of H_2O_2 is referred to as "hydrogen peroxide solution" or "liquid source."

<Substrate Loading Step S**10**>

First, a predetermined number of wafers **200** are charged into the boat **217** (wafer charging). The boat **217** holding the wafers **200** is elevated by the boat elevator and loaded into the processing vessel **203** (into the process chamber **201**) (boat loading). With the boat **217** loaded, the seal cap **219** seals the lower end opening (furnace opening) of the processing furnace **202**.

<Pressure and Temperature Adjusting Step S**20**>

The vacuum pump **246** vacuum-exhausts the processing vessel **203** such that the inner pressure of the processing vessel **203** is adjusted to a desired pressure (vacuum level). The oxygen-containing gas is supplied into the processing vessel **203** via the supply hole **501***b* of the oxygen-containing gas supply system. Preferably, the oxygen-containing gas is supplied into the processing vessel **203** after being heated to a temperature ranging from 100° C. to 120° C. by the heater **602***e*. At this time, the inner pressure of the processing vessel **203** is measured by the pressure sensor **223**, and the opening degree of the APC valve **255** is feedback-controlled based on the measured pressure (pressure adjusting). Preferably, the inner pressure of the processing vessel **203** is adjusted such that the processing vessel **203** is not depressurized, for example, to a pressure ranging from 700 hPa to 1,000 hPa.

The first heater **207** heats the processing vessel **203** such that the temperature of the wafers **200** in the processing vessel **203** is adjusted to a desired first temperature ranging from 40° C. to 100° C., for example. The energization states of the first heating part **207***a* through the fourth heating part **207***d* of the first heater **207** are feedback-controlled based on the temperature measured by the first temperature sensor **263***a* through the fourth temperature sensor **263***d*, respectively, such that the wafers **200** in the processing vessel **203** are at the first temperature (temperature adjusting). The first heating part **207***a* through the fourth heating part **207***d* are controlled such that the temperatures of the first heating part **207***a* through the fourth heating part **207***d* are the same. The second heater **208** is controlled to adjust the inner temperature of the processing vessel **203** such that the process gas is not re-liquefied in the processing vessel **203**, particularly in the lower portion of the processing vessel **203**. Preferably, the second heater **208** heats the lower portion of the processing vessel **203** to a temperature ranging from 100° C. to 200° C.

The rotating mechanism **267** starts to rotate the boat **217** and the wafers **200** while the wafers **200** are heated. The rotation speed of the boat **217** is controlled by the controller **121**. The rotating mechanism **267** continuously rotates the boat **217** until at least the modifying step S**30**, which will be described later, is complete.

<Modifying Step S**30**>

When the wafer **200** is heated to a first temperature, and the boat **217** is rotated at a predetermined speed, the liquid source (hydrogen peroxide solution) is supplied to the vaporizer **100** by the liquid source supply system **300**. Specifically, the flow rate of the liquid source supplied by the liquid source supply system **300** is adjusted by the LMFC **303**. After the flow rate of the liquid source is

adjusted, the liquid source is supplied into the vaporizer vessel **101** of the vaporizer **100** via the dripping nozzle **107** by opening the valve **302**. The liquid source supplied to the vaporizer **100** is dropped onto the inner bottom surface of the vaporizer vessel **101** through the dripping nozzle **107**. Since the vaporizer vessel **101** is heated by the vaporizer heater **103** to a desired temperature (for example, 150° C. to 170° C.), the droplets of the liquid source (hydrogen peroxide solution) that comes in contact with the inner bottom surface of the vaporizer vessel **101** is instantaneously heated and evaporated to a gas.

The process gas, which is the gas obtained from the liquid source by vaporization, is supplied to the wafers in the process chamber by opening the valve **289***b* via the exhaust port **104**, the process gas supply pipe **289***a*, the valve **289***b*, the process gas supply nozzle **501***a*, and the supply hole **501***b* of the process gas supply nozzle **501***a*. The H_2O_2 gas contained in the process gas acts as a reactive gas. The H_2O_2 gas contained in the process gas reacts with the silicon-containing film on the wafer to modify (oxidize) the silicon-containing film, thereby forming a SiO film.

With the process gas being supplied into the processing vessel **203**, the inner atmosphere of the processing vessel **203** is exhausted by the vacuum pump **246**. Specifically, the APC valve **255** is opened and the vacuum pump **246** is operated, and the gas exhausted from the processing vessel **203** flows through the gas exhaust pipe **231** and the gas concentration meter **600**. After a predetermined time has elapsed, the valve **289***b* is closed and the supply of the process gas into the processing vessel **203** is stopped. After another predetermined time has elapsed, the APC valve **255** is closed and the exhaust of the inner atmosphere of the processing vessel **203** is stopped.

During the supply of the process gas into the processing vessel **203**, the APC valve **255** may be closed to pressurize the processing vessel **203**. By pressurizing the processing vessel **203**, the atmosphere of the process gas in the processing vessel **203** can be more uniform.

While the embodiment is described by way of an example wherein hydrogen peroxide solution is supplied to the vaporizer **100** as a liquid source and the process gas containing H_2O_2 is supplied into the processing vessel **203**, the above-described technique is not limited thereto. The above-described technique may also be applied, for example, when a liquid including ozone (O_3) and a liquid such as water (H_2O) are used as a liquid source.

When the process gas is produced by the vaporizer **100** without an oxygen-containing gas supplied into the processing vessel **203**, the processing of the wafers **200** at different locations of the boat (e.g. wafers **200** at upper portion and lower portion of the boat) may not be uniform Moreover, the amount of impurities may increase, thereby degrading the film quality. Therefore, an oxygen-containing gas may be supplied into the processing vessel **203** via the oxygen-containing gas supply nozzle **502***a* and the supply port **502***b* before vaporizing the liquid source into the process gas containing H_2O_2 by the vaporizer **100** in order to improve process uniformity among the wafers **200** accommodated in the processing vessel **203**.

After the completion of the modifying step S**30** is complete, N_2 gas (inert gas) serving as a purge gas is supplied into the processing vessel **203** while the vacuum pump **246** vacuum-exhausts the inner atmosphere of the processing vessel **203** with the APC valve **255** open. According to the embodiment, inert gas such as N_2 gas and rare gases such as helium (He) gas, neon (Ne) gas and argon (Ar) gas may be used as the purge gas. The purge gas promotes the exhaust of residual process gas from the processing vessel **203**.

<Drying Step S**40**>

After the modifying step S**30** is completed, the temperature of the wafer **200** is elevated to a predetermined second temperature. The second temperature is higher than the first temperature and is equal to or lower than the temperature of the pre-baking step T**30**. The second temperature is, for example, 150° C. After the temperature of the wafer **200** is elevated to the second temperature, the wafer **200** and the inside of the processing vessel **203** are gradually dried while maintaining the second temperature. As a result, by-products such as ammonia, ammonium chloride, carbon and hydrogen, which are desorbed from the polysilazane film, impurities such as gas from the solvent, and impurities from to H_2O_2 are prevented from reattaching to the wafer **200** while drying the wafer **200**.

Preferably, the flow rate of the oxygen-containing gas may be adjusted to a second flow rate greater than the first flow rate before or while elevating the temperature of the wafer **200** to the second temperature. The flow rate of the oxygen-containing gas ranges, for example, from 10 slm to 40 slm. By adjusting the flow rate of the oxygen-containing gas as described above before or while elevating the temperature of the wafer **200** is elevated to the second temperature, the efficiency of removing the impurities is improved.

<Post-Baking Step S**50**>

After the drying step S**40** is completed, the temperature of the wafer **200** is elevated to a temperature higher than the second temperature of the drying step S**40** under an atmosphere containing at least one of nitrogen, oxygen and argon to remove hydrogen remaining in the SiO film. As a result, a high quality SiO film with low hydrogen content is obtained. By performing the post-baking step S**50**, the SiO film with improved quality can be obtained for a device manufacturing process requiring a high quality oxide film such as STI. The post-baking step S**50** may be omitted in device manufacturing processes requiring a high quality oxide film when the manufacturing throughput is prioritized.

<Cooling and Returning to Atmospheric Pressure Step S**60**>

After the drying step S**40** or the post-baking step S**50** are completed, the particles or impurities remaining in the processing vessel **203** are removed by opening the APC valve **255** and exhausting the processing vessel **203**. After vacuum exhaust, the APC valve **255** is closed and the inner pressure of the processing vessel **203** is returned to atmospheric pressure. Thereafter, the wafer **200** and the processing vessel **203** are heated to remove the particles and impurities still remaining after the vacuum exhaust, the gas desorbed from the wafer **200** and the residual impurities contained in the hydrogen peroxide solution. It is preferable to the wafer **200** and the processing vessel **203** are heated under atmospheric pressure because the heat capacity of the processing vessel **203** is increased and the wafer **200** and the processing vessel **203** are more uniformly heated. After the inner pressure of the processing vessel **203** is returned to atmospheric pressure and a predetermined time has elapsed, the temperature of wafer **200** is lowered until a predetermined temperature (e.g., a temperature at which the wafer can be unloaded) is reached.

The heating by the second heater **280** is lowered while the wafer **200** is cooled. Specifically, the electrical power supplied to the second heater **280** is stopped to lower the heating by the second heater **280**. The heating by the second heater **280** is stopped while the wafer **200** is cooled to maintain the quality of the films formed on the surface of the wafers **200**

uniform among the wafers **200** disposed at different location of the boat. In addition, the adsorption of particles, impurities and the gas generated from the wafer **200** in the processing vessel **203** are suppressed from adsorbing to the furnace opening.

During the cooling of the wafer **200**, a cooling gas supplied via a cooling gas supply pipe **249** and having a flow rate thereof controlled by the MFC **251** may be supplied into a space **260** between the processing vessel **203** and the insulating member **210** and then exhausted through a cooling gas exhaust pipe **253** by opening shutters **252**, **254** and **256** and operating a blower **257**. N_2 gas, air, rare gas such as He gas, Ne gas and Ar gas and combinations thereof may be used as the cooling gas. The space **260** can be rapidly cooled by supplying the cooling gas as well as the processing vessel **203** and the first heater **207** provided in the space **260**. The wafer **200** in the processing vessel **203** can also be cooled in a shorter time.

Alternatively, with the shutters **254** and **256** closed, the cooling gas such as N_2 gas may be supplied into the space **260** through the cooling gas supply pipe **249** to fill the space **260** with the cooling gas for cooling the space **260**. The cooling gas in the space **260** may then be exhausted through the cooling gas exhaust pipe **253** by opening the shutters **254** and **256** and operating the blower **257**.

<Substrate Unloading Step S**70**>

Thereafter, the seal cap **219** is lowered by the boat elevator and the lower end of the processing vessel **203** is opened. The boat **217** charged with the processed wafers **200** is unloaded from the processing vessel **203** through the lower end of the processing vessel (boat unloading). The processed wafers **200** are then discharged from the boat **217** (wafer discharging). The substrate processing according to the embodiment is now complete.

(4) Measurement and Control of Consumption of Reactive Gas in Process Chamber

Next, the process of measuring (calculating) the amount of the reactive gas (H_2O_2 gas according to the embodiment) consumed in the process chamber **201** using the gas concentration meters **500** and **600** will be described. In the modifying step S**30**, the process gas containing H_2O_2 gas as a reactive gas is supplied into the process chamber **201** via the process gas supply pipe **289***a*. The gas concentration meter **500** provided in the process gas supply pipe **289***a* measures the concentration of the reactive gas contained in the process gas flowing through the process gas supply pipe **289***a*. Specifically, the light emitter **520** emits near-infrared ray to the process gas passing through the cell **540**, and the light receiver **530** receives near-infrared ray that has passed through the process gas. The near-infrared rays received by the light receiver **530** are transmitted to the analyzer **510**. The analyzer **510** calculates the concentration of the reactive gas in the process gas passing through cell **540** by analyzing the spectrum of the received near-infrared rays and evaluating the magnitude of unique spectral component of the light beam that has passed through the reactive gas in the process gas. The spectrum can be analyzed using known general techniques.

In the modifying step S**30**, the vacuum pump **246** evacuates the inner atmosphere of the processing vessel **203**. The gas concentration meter **600** installed at the gas exhaust pipe **231** measures the concentration of the reactive gas contained in the exhaust gas flowing through the gas exhaust pipe **231**. Specifically, the light emitter **620** emits near-infrared ray to the exhaust gas passing through the cell **640**, and the light receiver **630** receives near-infrared ray that has passed through the exhaust gas. The near-infrared rays received by the light receiver **630** are transmitted to the analyzer **610**. Similar to the analyzer **510**, the analyzer **610** calculates the concentration of the reactive gas in the exhaust gas passing through cell **640** by analyzing the spectrum of the received near-infrared rays and evaluating the magnitude of unique spectral component of the light beam that has passed through the reactive gas in the exhaust gas. The analyzer **610** analyzed the spectrum using known general techniques similar to the analyzer **510**. The data representing the concentrations (concentration data) of the reactive gas in the process gas and the reactive gas in the exhaust gas generated by the analyzers **510** and **610**, respectively, are preferably transmitted to the controller **121** at predetermined time intervals.

The controller **121** receives the concentration data acquired by the gas concentration meters **500** and **600** and sequentially stores the received concentration data in the components such as the storage **121***c*. The controller **121** may inform the user of the gas concentrations via the input/output device **122**. The controller **121** calculates the amount of the reactive gas consumed in the process chamber **201** (hereinafter, referred to as "amount of consumed reactive gas") based on the received gas concentration. Specifically, the controller **121** calculates the difference between the gas concentrations obtained by the gas concentration meters **500** and **600** as a value indicating the amount of consumed reactive gas. The controller **121** is also capable of further calculating the difference using a predetermined coefficient or using other data acquired separately as the amount of consumed reactive gas. The calculated amount of consumed reactive gas is sequentially recorded in the components such as the storage device **121***c* and is also notified to the user via the input/output device **122**. The calculated amount of consumed reactive gas may be recorded and notified to reflect the processing speed (reaction speed) of the wafer **200**.

The controller **121** is capable of storing, in the component such as the storage **121***c*, the cumulative amount of consumed reactive gas calculated from the time point at which the reactive gas is first supplied to the wafer **200** in the modifying step S**30**, and is also capable of informing the user of the cumulative amount of consumed reactive gas via the input/output device **122**. The cumulative amount of consumed reactive gas may be recorded and notified to reflect the progress of the processing of the wafer **200**.

While the embodiment is described by way of an example wherein the controller **121** calculates parameters such as the amount of consumed reactive gas. However, a dedicated calculation unit for calculating a parameter such as an amount of consumed reactive gas may be employed instead of the controller **121**. The calculation unit may be electrically connected to the controller **121** and can be controlled by the controller **121**.

One or more advantageous effects described below are provided according to the embodiment.

(a) The gas concentration meters **500** and **600** are provided at the process gas supply pipe **289***a* for supplying the gas to the process chamber **201** and the gas exhaust pipe **231** for exhausting the gas from the process chamber **201**, respectively. The amount of the reactive gas consumed in the process chamber **201** may be determined based on the concentrations of reactive gases in the process gas and the exhaust gas measured by the gas concentration meters **500** and **600**, respectively. The amount of the reactive gas participated in the chemical reaction between the reactive gas and the wafer **200** can be determined based on the amount of consumed reactive gas.

(b) Conventionally, the thickness of the film formed on the wafer **200** was measured in order to determine the progress of substrate processing (e.g. the progress of the oxidation of the silicon-containing film by H_2O_2 gas). Therefore, conventionally, it was problematic that the progress is difficult to be determined during the substrate processing, that the thickness of the film should be measured directly, and that the thickness of the film cannot be measured accurately when the thickness of the film is thin. It can be regarded that the amount of consumed reactive gas accumulated from the time point at which the process gas is first supplied to the wafer **200** (the cumulative amount of consumed reactive gas) is proportional or is likely to be proportional to the progress of the wafer processing. Therefore, by measuring the cumulative amount of consumed reactive gas, it is possible to determine the progress of the processing of the wafer **200** at desired time point. By comparing the cumulative amounts of consumed reactive gas of processing lots with one another, the processing quality can be constantly managed for each processing lot.

(c) It can be regarded that the amount of reactive gas consumed per unit time is proportional or is likely to be proportional to the speed of the processing of the wafer **200** (the speed of the oxidation of the silicon-containing film by H_2O_2 gas according to the embodiment). Therefore, the speed of the processing of the wafer **200** can be determined by measuring the amount of consumed reactive gas per unit time. The processing quality can be maintained for each processing lot by comparing the amount of the reactive gas consumed per unit time or the change thereof among the processing lots.

(d) The amount of consumed reactive gas generally increases or decreases depending on the number of wafers **200** processed in the processing vessel **203**. According to the embodiment, it is possible to determine the amount of consumed reactive gas (the amount of consumed reactive gas per unit time and the history data thereof) per batch of wafers **200** in each processing lot. Therefore, conditions such as the supplied amount of the process gas can be optimized according to the number of wafers **200**.

According to the embodiment, the examples of processing described below are performed based on the calculated amount of consumed reactive gas.

<First Example of Processing>

As described above, since the speed of the processing of the wafer **200** can be determined by measuring the amount of consumed reactive gas per unit time, the speed of the processing of the wafer **200** can be feedback-controlled based on the measured amount of consumed reactive gas. The amount of the process gas produced by the vaporizer **100** may be adjusted by controlling the LMFC **303** and the MFC **601***b* based on the calculated amount of consumed reactive gas per unit time, thereby controlling the flow rate of the process gas supplied into the process chamber **201**. As a result, the speed of the processing of the wafer **200** can be controlled. Specifically, when the amount of consumed reactive gas per unit time is determined to be lower than a predetermined value, the flow rate of the process gas may be increased. Similarly, when the amount of consumed reactive gas per unit time is determined to be higher than the predetermined value, the flow rate of the process gas may be decreased.

<Second Example of Processing>

When the amount of consumed reactive gas per unit time decreases to a predetermined level, it can be regarded that the chemical reaction occurring at the wafer **200** (the reaction of oxidizing the silicon-containing film by the H_2O_2 according to the embodiment) is saturated, and the modifying step can be terminated. As a result, the processing time can be shortened and the throughput can be improved by stopping the supply of the process gas.

<Third Example of Processing>

As described above, by measuring the cumulative amount of consumed reactive gas, the progress of the processing of the wafer **200** at each time point of substrate processing can be determined. According to the third example of processing, when the cumulative amount of consumed reactive gas reaches a predetermined level, the modifying step is terminated. As a result, the processing time can be shortened and the throughput can be improved.

<Fourth Example of Processing>

When the amount of consumed reactive gas per unit time is determined to be either lower than or higher than a predetermined value, an alarm may be issued via components such as the input/output device **122** to inform the user of possible fault in the processing of wafers in the process chamber **201**.

<Fifth Example of Processing>

When the cumulative amount of consumed reactive gas is determined to be either lower than or higher than a predetermined value at the end of the modifying step, an alarm may be issued via components such as the input/output device **122** to inform the user of possible fault in the processing of a processing lot.

<Sixth Example of Processing>

Generally, the amount of consumed reactive gas generally increases or decreases depending on the number of wafers **200** processed in the processing vessel **203**. According to the sixth example of processing, an optimal amount of the process gas may be determined per batch of wafers **200** in each processing lot. Specifically, the controller **121** records (logs) the history of the amount of consumed reactive gas per unit time for each processing lot in the component such as the storage device **121***c*. The controller **121** acquires the number of wafers **200** to be processed in the processing vessel **203** for each processing lot via the input/output device **122** or from the external memory device **123**. Subsequently, the controller **121** associates the amount of consumed reactive gas per unit time with the number of the wafers **200** for each processing lot. As a result, the history data (pattern) of the amount of consumed reactive gas per unit time with respect to the number of wafers **200** can be obtained. The controller **121** optimizes the amount of supplied process gas by adjusting the amount of the process gas based on the history data of the amount of consumed reactive gas per unit time associated with the number of the wafers **200**. The controller **121** refers to the history data of the amount of consumed reactive gas of the previous process lot having the same number of wafers **200**, and controls the amount of the supplied process gas such that the amount of the supplied process gas is no less than that of the process in the history data. As a result, under-supply of the process gas can be prevented as well as over-supply of the process gas.

<Seventh Example of Processing>

When the difference between the history data (pattern) of the reactive gas consumption per unit time of current processing lot and the history data (pattern) of the reactive gas consumption per unit time of the previous processing lot of the same number of wafers **200** is out of a predetermined range, an alarm may be issued via components such as the

input/output device **122** to inform the user of possible fault in the processing of wafers in the process chamber **201**.

Other Embodiments

While the technique is described in detail by way of the embodiment and examples, the above-described technique is not limited thereto. The above-described technique may be modified in various ways without departing from the gist thereof.

For example, according to the above-described embodiments, a gas containing H_2O_2 gas is used as the process gas. However, the above-described technique is not limited thereto. That is, the process gas may be a gas produced from vaporizing a solution of a solid source (reactant) or a liquid source (reactant) dissolved in a solvent at room temperature (reactant dissolved liquid). When the boiling point of the source differs from that of the solvent, the above-described advantageous effects can be easily obtained. In addition, the above-described technique is not limited to the case where the concentration of the source increases when the process gas is re-liquefied. The above-described technique may be applied to a case where the concentration of the source decreases when the process gas is re-liquefied. According to the above-described technique, the process gas having uniform concentrated in the processing vessel **203** may be obtained even when the concentration of the source decreases due to re-liquefaction.

For example, according to the above-described embodiments, hydrogen peroxide gas is used as the process gas. However, the above-described technique is not limited thereto. H_2O gas produced by the reaction of a gas containing hydrogen (hydrogen-containing gas) such as hydrogen (H_2) gas and a gas containing oxygen (oxygen-containing gas) such as oxygen (O_2) gas. Water vapor generated by heating water may also be used as the process gas.

For example, according to the above-described embodiments, the process gas is produced by heating and vaporizing a liquid source. However, the above-described technique is not limited thereto. The above-described technique may be applied when processing a substrate in a process chamber by supplying a process gas containing a predetermined reactive gas into the process chamber.

The H_2O_2 contained in the process gas described above may be H_2O_2 molecules or a cluster of H_2O_2 molecules. When hydrogen peroxide solution is used to generate a gas containing H_2O_2, H_2O_2 molecules or the cluster of H_2O_2 molecules may be separated from the hydrogen peroxide solution. H_2O_2 may be in a mist state in which the clusters are combined.

When a gas (water vapor) produced by vaporizing water (liquid source) is used as the process gas, the water vapor supplied to the wafer **200** may be H_2O molecules or a cluster of H_2O molecules. When water is converted water from a liquid phase to a gaseous phase, H_2O molecules or the cluster of H_2O molecules may be separated. H_2O may be in a mist state in which the clusters are combined.

While the embodiment is described by way of an example wherein the wafer having the polysilazane film is processed, the above-described technique is not limited thereto. The above-described technique may also be applied when a wafer having thereon a film containing a silazane bond (—Si—N—). The above-described technique may also be applied when a coating film including materials such as hexamethyldisilazane (HMDS), hexamethylcyclotrisilazane (HMCTS), polycarbosilazane and polyorganosilazane.

While the embodiment is described by way of an example wherein the wafer having thereon a spin-coated and pre-baked film containing a silazane bond is processed, the above-described technique is not limited thereto. The above-described technique may also be applied when oxidizing non-prebaked silicon-containing film formed by CVD method from silicon sources such as monosilane (SiH_4) gas and trisilylamine (TSA) gas. Particularly, the non-prebaked silicon-containing film may be formed by flowable CVD which enables the filling of grooves with high aspect ratio with the silicon-containing film. The silicon-containing film in the grooves may be subjected to oxidation process or annealing process according to the above-described technique.

According to the above-described embodiments, the substrate processing using a substrate processing apparatus having vertical type processing furnace is exemplified. However, the above-described technique is not limited thereto. The above-described technique may also be applied to the substrate processing using a single type substrate processing apparatus, a substrate processing apparatus having hot wall type processing furnace, a substrate processing apparatus having cold wall type processing furnace and a substrate processing apparatus capable of processing the wafers **200** by activating the process gas.

While the embodiment is described by way of an example wherein the concentration of the H_2O_2 gas is acquired by the gas concentration meter according to the analysis described above, the above-described technique is not limited thereto. The above-described technique may also be applied when the concentration of the H_2O_2 gas is acquired according to other well-known analyses and the same advantageous effects are obtained.

According to the technique described herein, the progress of the reaction between the substrate and the reactive gas contained in the process gas in the process chamber can be acquired, monitored and recorded during the substrate processing.

What is claimed is:

1. A substrate processing apparatus comprising:
a process chamber capable of accommodating a substrate;
a process gas supply system configured to supply a process gas into the process chamber via a process gas supply pipe;
an exhaust pipe configured to exhaust an inner atmosphere of the process chamber;
a gas concentration sensor configured to be capable of detecting a first concentration which is a concentration of the process gas in the process gas supply pipe or detecting a second concentration which is a concentration of the process gas contained in an exhaust gas in the exhaust pipe or detecting both of the first concentration and the second concentration; and
a controller configured to be capable of performing: (a) controlling the process gas supply system to start a supply of the process gas into the process chamber at a predetermined flow rate; and (b) controlling the process gas supply system to reduce the predetermined flow rate into the process chamber or to stop the supply of the process gas into the process chamber when an amount of the process gas consumed in the process chamber, which is calculated based on a value of the first concentration and a value of the second concentration detected by the gas concentration sensor, becomes equal to or lower than a predetermined value.

2. The substrate processing apparatus of claim **1**, wherein the gas concentration sensor comprises:

a first gas concentration sensor configured to detect the first concentration of the process gas in the process gas supply pipe; and

a second gas concentration sensor configured to detect the second concentration of the process gas contained in the exhaust gas in the exhaust pipe.

3. The substrate processing apparatus of claim **2**, wherein the first gas concentration sensor comprises: a cell where through the process gas passes; a light emitter configured to irradiate a near-infrared ray to the process gas passing through the cell; a light receiver configured to receive the near-infrared ray irradiated to the process gas; and a calculator configured to calculate the first concentration based on a spectrum of the near-infrared ray received by the light receiver.

4. The substrate processing apparatus of claim **1**, wherein the gas concentration sensor obtains the value of the first concentration and the value of the second concentration at a constant interval.

5. The substrate processing apparatus of claim **1**, further comprising a valve provided at the process gas supply pipe,

wherein the controller is further configured to control the valve to start the supply of the process gas into the process chamber by opening the valve.

6. The substrate processing apparatus of claim **1**, wherein the controller is configured to calculate the amount of the process gas consumed in the process chamber based on a difference between the values of the first concentration and the second concentration in (b).

7. The substrate processing apparatus of claim **1**, further comprising an input/output device,

wherein the controller is further configured to control the input/output device to inform a user of a cumulative amount of the process gas consumed in the process chamber by accumulating the amount of the process gas consumed in the process chamber calculated in (b) from a start of the supply of the process gas into the process chamber.

8. The substrate processing apparatus of claim **7**, wherein the controller is further configured to control the input/output device to inform the user of the cumulative amount as a progress of processing of the substrate.

9. The substrate processing apparatus of claim **1**, wherein the controller is further configured to control the process gas supply system to stop the supply of the process gas into the process chamber when the cumulative amount calculated in (b) reaches a predetermined value.

10. The substrate processing apparatus of claim **1**, wherein the controller is further configured to record a cumulative amount of the process gas consumed in the process chamber by accumulating the amount of the process gas consumed in the process chamber calculated in (b) from a start of the supply of the process gas into the process chamber in a memory device.

11. The substrate processing apparatus of claim **1**, further comprising a process gas generator configured to generate and supply the process gas including hydrogen peroxide to the process gas supply pipe.

12. The substrate processing apparatus of claim **1**, further comprising a vaporizer configured to vaporize hydrogen peroxide solution to produce the process gas and supply the process gas to the process gas supply pipe.

13. A substrate processing method, comprising:

(a) supplying a process gas into a process chamber via a process gas supply pipe connected thereto with a substrate accommodated in the process chamber and exhausting the process gas from the process chamber via an exhaust pipe connected thereto;

(b) detecting a first concentration which is a concentration of the process gas in the process gas supply pipe or a second concentration which is a concentration of the process gas contained in an exhaust gas in the exhaust pipe; and

(c) controlling a process gas supply system to reduce a predetermined flow rate into the process chamber or to stop a supply of the process gas into the process chamber when an amount of the process gas consumed in the process chamber, which is calculated based on a value of the first concentration and a value of the second concentration detected by a gas concentration sensor, becomes equal to or lower than a predetermined value.

14. A method of manufacturing a semiconductor device, comprising the substrate processing method of claim **13**.

15. A non-transitory computer-readable recording medium storing a program that causes, by a computer, a substrate processing apparatus to perform:

(a) supplying a process gas into a process chamber via a process gas supply pipe connected thereto with a substrate accommodated in the process chamber and exhausting the process gas from the process chamber via an exhaust pipe connected thereto;

(b) detecting a first concentration which is a concentration of the process gas in the process gas supply pipe or a second concentration which is a concentration of the process gas contained in an exhaust gas in the exhaust pipe; and

(c) controlling a process gas supply system to reduce a predetermined flow rate into the process chamber or to stop a supply of the process gas into the process chamber when an amount of the process gas consumed in the process chamber, which is calculated based on a value of the first concentration and a value of the second concentration detected by a gas concentration sensor, becomes equal to or lower than a predetermined value.

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